



On the search of size- and shape-controlled metal chalcogenide cluster compounds

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ABSTRACT

Hg(TePh)₂ (Ph = phenyl) reacts with CdI₂(PPh₃)₂, PPhMe₂ (Me = methyl), and PPh₃/Zn(NO₃)₂·4H₂O to give the compounds [Hg₄(TePh)₇IPy]_n (Py = pyridine) (**1**), [Hg₈Te(TePh)₁₄(PPhMe₂)₂]·0.5DMF (DMF = dimethylformamide) (**2**) and [Hg₁₁(TePh)₁₈Te₂Py₃]_n (**3**).

While **1** and **3** assemble polymeric clusters, **2** can be described as a super tetrahedron with a Te²⁻ ion located in the center. The geometric topology of cluster **3**, together with some experimental evidences, suggests that its core is attained by the spontaneous fusion of clusters **1** and **2**.

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1. Introduction

The growth patterns of nanoclusters in solution and the management of the processes which rule the synthesis of bulky clusters compounds are important and exciting subject matters. Thus, research towards understanding the manipulation of the self-assembly processes of *tectons* (building blocks) [1] that raise the formation of chains, layers or grids, has become attractive and useful to enable the design of multifunctional materials [2,3].

In contrast to IIb–VI molecules with skeleton atoms ZnS [4,5], ZnSe [6], ZnTe [7], CdS [8–12] and CdSe [13,14], chalcogenide clusters compounds with mercury are rare, although they enclose interesting properties as bulk- or nano-materials. The alloy Cd_{1-x}Hg_xTe is a useful material for long-wavelength infrared detector technologies, and HgTe nanoparticles were proposed to act as potential amplifiers for telecommunication tools [15,16]. Mercury chalcogenide compounds have found considerable use in industry, especially as low band gap semi-conductors, in photo-voltaic applications and IR detection devices [17].

The synthesis and structural characterization of metal chalcogenide molecules with defined size and structure provide an interesting approach to this class of materials [18]. We have already shown that (PhE)₂Hg (Ph = phenyl; E = Se, Te) carries great weight as precursor for the synthesis of binary (bimetallic) and ternary nanoclusters and polymers (see next section). Presently, we

attempt to find patterns which allow the development of building blocks units, whose variable assembly leads to the achievement of clusters with different structural characteristics.

With the aim to demonstrate some further interesting peculiarities regarding the syntheses of Hg–chalcogenide clusters, we describe the preparation and the structural features of the new clusters compounds [Hg₄(TePh)₇IPy]_n (Py = pyridine) (**1**), [Hg₈Te(TePh)₁₄(PPhMe₂)₂]·0.5DMF (Me = methyl; DMF = dimethylformamide) (**2**), and [Hg₁₁(TePh)₁₈Te₂Py₃]_n (**3**). We discuss also some possible patterns associated to the growth of the new products.

2. Results and discussion

2.1. Structure

Fig. 1 shows the polymeric structure of [Hg₄(TePh)₇IPy]_n (**1**), attained by adamantanoid moieties of the cluster [Hg₄(TePh)₆IPy], linked through μ-TePh bridges along the crystallographic axis z. In each single unit of the cluster [Hg₄(TePh)₇IPy] the geometry of the Hg^{II} atoms is a distorted tetrahedron and the Hg^{II} atoms are connected through asymmetric [μ-TePh]⁻ bridges to form the adamantanoid structures. Atoms Hg3 and Hg4 are bound to four Te atoms, while atoms Hg1 and Hg2 are linked to three Te atoms. Their coordination spheres are completed by one pyridine molecule (Hg1) and one iodide ligand (Hg2), respectively. The Hg–Te distances in **1** range within 2.7065(6)–2.8745(6) Å, and the further mercury bonds are Hg2–I1 = 2.7967(8) Å and Hg1–N1 = 2.566(7) Å. Similar structures with M–EPH (E = S, M = Zn [19,20], Cd

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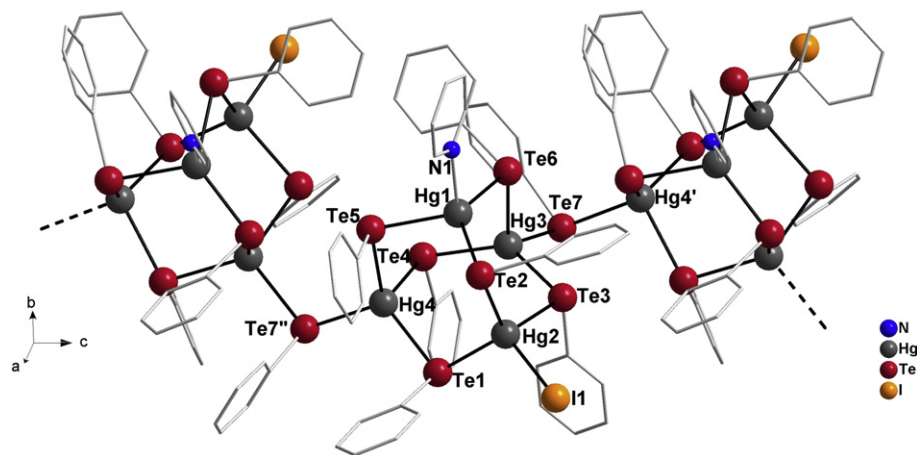


Fig. 1. Molecular and polymeric structure of $[\text{Hg}_4(\text{TePh})_7\text{IPy}]_n$ (**1**) (hydrogen atoms omitted for clarity). Symmetry transformations used to generate equivalent atoms: (') $x, 1.5-y, -0.5+z$; (") $x, 1.5-y, 0.5+z$.

[21–24], Fe [6], Co [25,26], Mn [27]; $E = \text{Se}$, $M = \text{Hg}$ [28], Zn [29] have been reported. The molecular structure of $[\text{Hg}_8\text{Te}(\text{TePh})_{14}(\text{PPhMe}_2)_2] \cdot 0.5\text{DMF}$ (**2**) is represented in Fig. 2. The core unit of **2**, $\text{Hg}_8(\mu_4\text{-Te})\text{Te}_{14}$, can be described as a tetrahedron with a $\mu_4\text{-Te}^{2-}$ ion located in the center. Four Hg atoms are directly bound to the Te^{2-} ion in a tetrahedral mode. To each of the four Hg atoms three PhTe moieties are bound. Each Hg atom presents an approximate tetrahedral geometry. The twelve PhTe moieties are bridged by four additional Hg atoms to close the $P1$ -type super tetrahedron [30]. The tetrahedral geometry of the four external Hg atoms is completed by two PhTe groups and two PPhMe_2 ligands. The Hg–Te bond distances for **2** range within 2.7179(9) – 2.9060(8) Å and the Hg–P bonds measure 2.560(3) Å and 2.580(3) Å.

The polymeric structure of $[\text{Hg}_{11}(\text{TePh})_{18}\text{Te}_2\text{Py}_3]_n \cdot n\text{Py}$ (**3**), represented in Fig. 3, consists of $[\text{Hg}_{11}(\text{TePh})_{18}\text{Te}_2\text{Py}_3]$ clusters connected by single Te bridges along the crystallographic axis z . The cores of **3** are linked through single tellurium bridges in the crystallographic direction z with the distances $\text{Te1-Hg1} = 2.9915(19)$ and $\text{Te1-Hg5}' = 2.7881(19)$ Å. Although in general a linear

coordination is very unusual for chalcogen ligands, the refinement of the Te1 site, carefully performed using anisotropic displacement parameters, showed a crystallographic threefold axis passing through the atoms Hg1, Te1 and Hg5'. In fact, the Te1-ellipsoid is almost twice bigger than the others Te ellipsoids, and this can be explained with basis on the size of the blocks in between of which the Te1 atom is squeezed.

Inside the core of **3**, each Hg^{II} atom has a quasi-tetrahedral coordination sphere. The atoms are bridged by eighteen $\mu_2\text{-TePh}$ groups and one $\mu_3\text{-Te}^{2-}$ anion. Three pyridine molecules complete the coordination sphere of the three mercury atoms located at the circumference of the cluster. The Hg– $\mu_2\text{-TePh}$ bond distances in **3** range within 2.7316(6) – 2.8846(8) Å and the Hg– $\mu_3\text{-Te}_2$ and Hg–N bonds measure 2.7548(7) and 2.550(9) Å, respectively.

2.2. Synthetic considerations

The reaction of $(\text{PhE})_2\text{Hg}$ with HgX_2 ($X = \text{Cl}, \text{Br}, \text{I}$) in coordinating solvents yields the unstable intermediary "PhEHgX", which seems to be the trigger for a great variety of reactions and structures, resumed in the Schemes 1 {A, B [31]; C [32]; D [33]; E, F [34]; G, H [35]; I, J, K [36]} and 2 {L, M [37]; N, O [38]; P, Q [37]}.

Most of these reactions involve a concurrence between two strong dipolar species L_1 and L_2 to stabilize the initial intermediary PhEHgX, and the end products depend upon the polarity of the reaction environment. We have experimentally observed that any mixtures of $\text{Hg}(\text{PhSe})_2$ with HgX_2 ($X = \text{Cl}, \text{Br}, \text{I}$) without any other ligands and in non-coordinating solvents (xylene or toluene, for example), do not react even under heating, since HgX_2 remains in the solid state and $\text{Hg}(\text{PhSe})_2$ dissociates partially in elemental Hg and $(\text{PhSe})_2$ [36]. We have carried out some previous reactions also with $(n\text{-C}_3\text{H}_7\text{Te})_2\text{Hg}$ [39], but the phenyl group in $(\text{PhTe})_2\text{Hg}$ has shown the best performance regarding the stabilization of the obtained clusters.

The critical aspect in the use of $\text{Hg}(\text{TePh})_2$ as starting reagent is the solvent choice. Monomeric compounds are formed in THF by decomposition with heating [40], while in DMSO or pyridine a series of clusters with mercury halide/phenyltelluride building blocks are produced [31,33,41]. The choice of adequate ligands or coordinating solvents is essential for stabilization of the mercury halide/ $[\text{Hg}(\text{TePh})_2\text{L}]$ building blocks in solution ($L =$ coordinating solvent or phosphines). The new interactions resulting from $[\text{Hg}(\text{TePh})_2\text{L}]$ building blocks and mercury halides in solution can be viewed as the driving forces of these reactions. Compounds **1**, **2** and

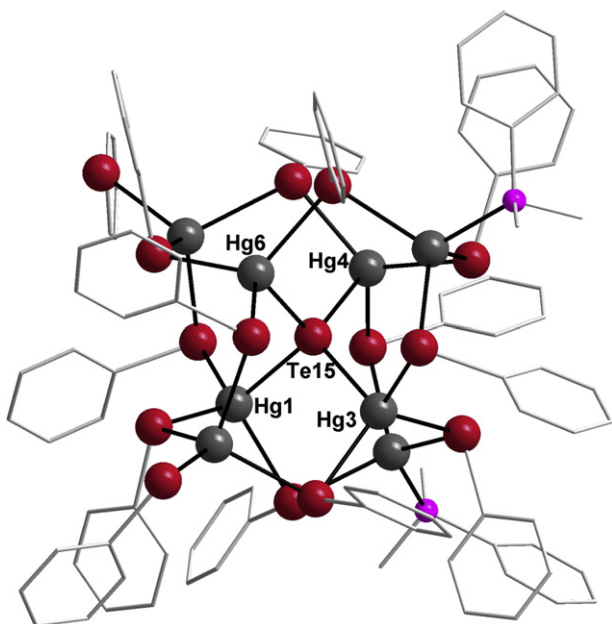


Fig. 2. Molecular structure of $[\text{Hg}_8\text{Te}(\text{TePh})_{14}(\text{PPhMe}_2)_2] \cdot 0.5\text{DMF}$ (**2**), without hydrogen atoms for clarity. Hg, Te and P atoms are shown as balls of arbitrary sizes.

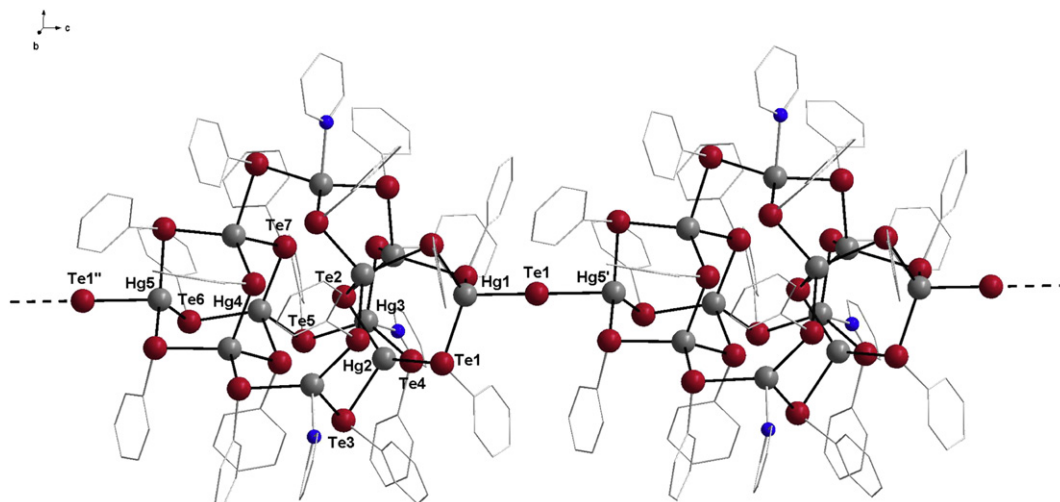


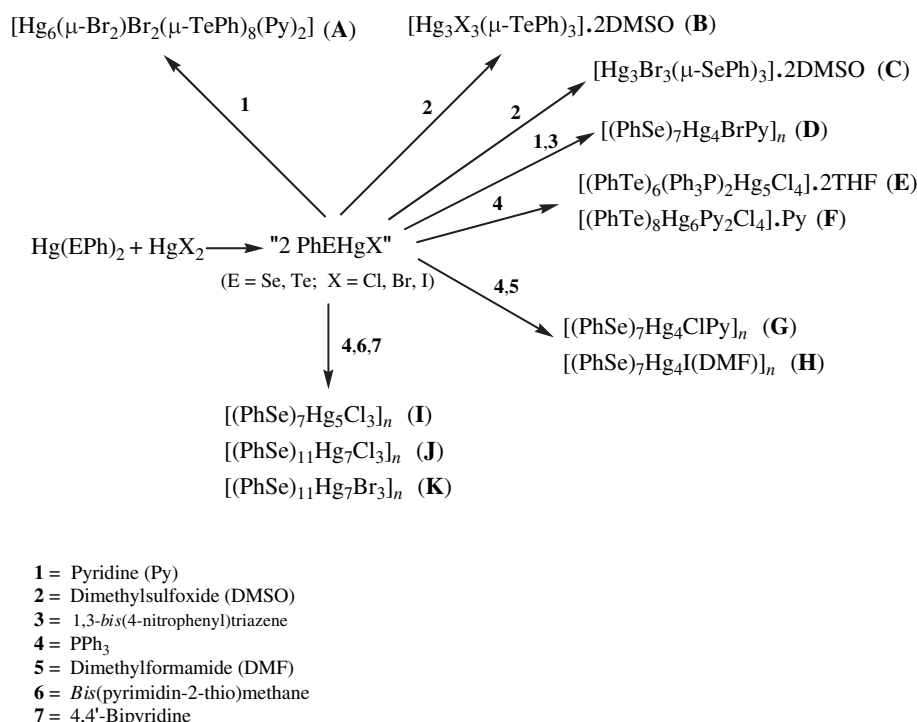
Fig. 3. Molecular and polymeric assembly of $[\text{Hg}_{11}(\text{TePh})_{18}\text{Te}_2\text{Py}_3]_n \cdot n\text{Py}$ (**3**). Hydrogen atoms and pyridine solvate molecules omitted for clarity. Symmetry operations used to generate equivalent atoms: (') $x, y, 1 + z$; (") $x, y, -1 + z$.

3 were obtained in accordance to the Scheme 3 (see next section). We have also observed that if some reactions parameters (stoichiometry, time, presence or not of co-ligands) are modified, the obtained products can differ outstandingly, with the formation of giant clusters, or, on the contrary, of polymer-forming adamantanoid structures. The topology of cluster **3** suggests that its core, $[\text{Hg}_{11}(\text{TePh})_{18}\text{Te}]^{2+}$, is formed by the fusion of clusters **1** and **2**.

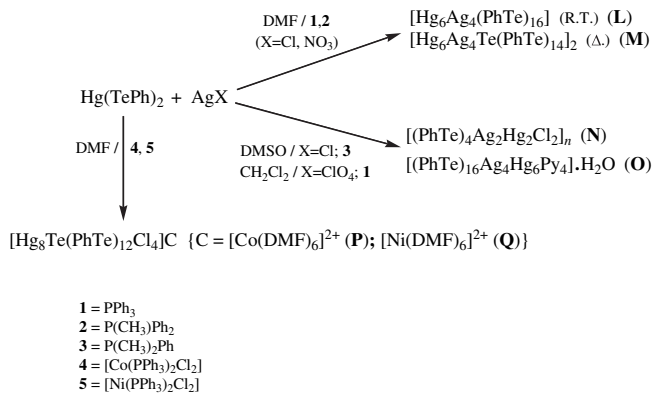
The adamantane-like unit $[\text{Hg}_4(\text{TePh})_6]$, outlined by the atoms Hg5, Te6 and Hg4 in Fig. 3 – similar to the adamantanoid moieties of compound **1** – is clearly coupled to the $[\text{Hg}_7(\text{TePh})_{12}\text{Te}]$ block (ending in Hg1), a block similar to an opened cluster **2**, which has a $[\text{Hg}_8(\text{TePh})_{14}\text{Te}]$ core. Thus, the fusion of the clusters has occurred also with improvement of the μ_4 -bridge function of the central Te15 atom of **2** (see Fig. 2) into a μ_3 function in Te2 (Fig. 3). If the sum of

the atoms of the cores of **1** and **2** are compared with that of the core of **3**, the difference is one $\text{Hg}(\text{TePh})_2$ unit less in **3**. The single Te1 atom was generated by a condensation between the $[\text{Hg1}-\text{TePh}]$ and $[\text{Hg5}-\text{TePh}]$ units, via elimination of TePh_2 molecules [42,43].

Compound **3**, in fact, seems to be the sum of **1** and **2**. It is well known that the nature of the organic ligands to the chalcogen, or the available P-donor or N-donor ligand to the metal, as well as addition of further (potential) ligand atoms (like I^-) strongly influence the structure of the observed product. However, it seems to be not clear so far, whether the reason for this is always located in the formation process of the clusters or whether it becomes crucial during crystallization – as the least soluble compound out of an equilibrium of co-existing species [44]. According to Scheme 3, compound **1** should be considered a thermodynamic product,



Scheme 1. Some binary clusters obtained from $(\text{PhE})_2\text{Hg}$ with HgX_2 (X = Cl, Br, I) {A, B [31]; C [32]; D [33]; E, F [34]; G, H [35]; I, J, K [36]}.



Scheme 2. Ternary clusters and complex salts obtained from (PhTe)₂Hg [L, M [37]; N, O [38]; P, Q [37]].

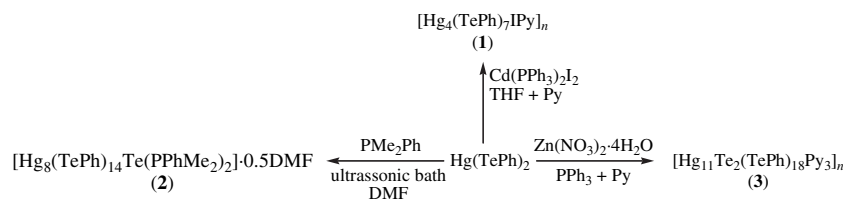
due to the presence of iodine (halogens stabilize the thermodynamically stable species). Compound **2** should be a kinetic product, since its formation occurs with energy supply and in the presence of PMe₂Ph. It is reasonable to assume that a significant amount of compounds **1** and **2** are stabilized in solution by the oxo-anion NO₃⁻, undergoing further combination to yield the more stable product **3**.

Chemical conversions of Hg clusters, as well as chemical and structural rearranges of Hg-organyltelluroate/selenolate clusters, are widely known and documented in the literature [34,41,45]. Finally, it must be mentioned that supplementary spectroscopic studies of the title compounds could not be performed because the pellets of the products have undergone rapid decomposition in the UV/VIS spectrometer with release of pyridine and PPh₃, probably due to photochemical processes strengthened by the air oxidation.

3. Experimental

3.1. Instrumentation

Crystallographic measurements were made on a Bruker Kappa Apex II CCD area detector with graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods (SHELXS-97) [46] and additional atoms were located in the difference Fourier map and refined on F² (SHELXL-97) [46]. Metal atoms were refined anisotropically; carbon atoms were refined isotropically; and hydrogen atoms as riding atoms at geometrically defined positions with isotropic thermal parameters 20% larger than their parent atoms. Refinement of the Te1 site in compound **3** was performed using anisotropic displacement parameters. Table 1 resumes the crystal data and the structure



Scheme 3. Reactions of Hg(TePh)₂ to yield **1**, **2** and **3**.

Table 1
Crystal data and structure refinement for **1**, **2** and **3**.

	1	2	3
Empirical formula	C ₄₇ H ₄₀ Hg ₄ INTe ₇	C ₁₀₃ H ₉₉ Hg ₈ NO ₂ Te ₁₅	C ₁₅₃ H ₁₃₅ Hg ₁₁ N ₉ Te ₂₀
Formula weight	2441.26	4947.49	6858.19
T (K)	295(2)	295(2)	293(2)
Radiation, λ (Å)	Mo–K α , 0.71073	Mo–K α , 0.71073	M–K α , 0.71073
Crystal system, space group	Monoclinic, P2 ₁ /c	Triclinic, P1	Trigonal, P $\bar{3}$
Unit cell dimensions a, b, c (Å)	a = 13.9646(3) b = 24.9542(5) c = 15.8998(3)	a = 14.1853(3) b = 14.5371(3) c = 15.7215(3)	a = 24.0296(3) b = 24.0296(3) c = 17.6698(4)
α, β, γ (°)	$\alpha = 90$ $\beta = 101.745(1)$ $\gamma = 90$	$\alpha = 82.012(1)$ $\beta = 70.661(1)$ $\gamma = 81.762(1)$	$\alpha = 90$ $\beta = 90$ $\gamma = 120$
V (Å ³)	5424.68(19)	3012.92(11)	8836.0(3)
Z, Calculated density (g cm ⁻³)	4, 2.989	1, 2.727	2, 2.578
Absorption coefficient (mm ⁻¹)	15.576	13.778	12.798
F(000)	4264	2182	6072
Crystal size (mm)	0.30 × 0.25 × 0.10	0.24 × 0.11 × 0.06	0.24 × 0.18 × 0.16
θ range (°)	2.72–30.52	2.75–30.64	2.05–29.00
Index ranges	–19 ≤ h ≤ 19 –35 ≤ k ≤ 35 –20 ≤ l ≤ 22	–20 ≤ h ≤ 20 –20 ≤ k ≤ 19 –22 ≤ l ≤ 22	–32 ≤ h ≤ 32 –15 ≤ k ≤ 32 –22 ≤ l ≤ 24
Reflections collected	80 025	83 612	90 370
Reflections unique	16 504 [R _{int} = 0.0587]	34 059 [R _{int} = 0.0477]	15 662 [R _{int} = 0.0713]
Completeness to theta max	99.6%	99.5%	99.8%
Absorption correction	Gaussian	Gaussian	Gaussian
Max. and min. transmission	1 and 0.502892	0.92 and 0.4366	1 and 0.353138
Refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on F ²
Data/restraints/parameters	16 504/0/457	34 059/579/945	15 662/0/466
Goodness-of-fit on F ²	1.023	0.824	1.055
Final R indices [I > 2σ(I)]	R ₁ = 0.0397 wR ₂ = 0.0831	R ₁ = 0.0366 wR ₂ = 0.0825	R ₁ = 0.0436 wR ₂ = 0.0982
R indices (all data)	R ₁ = 0.0970,	R ₁ = 0.0696,	R ₁ = 0.0770,
Largest diff. peak and hole (e.Å ⁻³)	1.388 and –2.481	0.743 and –1.220	4.667 and –5.944

refinement for the title compounds **1**, **2** and **3**. Elemental analysis were made by a Shimadzu EA 112 at the Universidade Federal de Santa Maria–Brazil and EDX (Energy Dispersive X-ray) analysis were made on a LEO mod 440, 20 keV at the Universidade de São Paulo – São Carlos – Brazil.

3.2. Synthetic procedures

The syntheses of $(\text{PhTe})_2$ and $\text{Hg}(\text{TePh})_2$ were performed in accordance with the literature [47]. The title compounds were prepared according to the Scheme 3:

3.2.1. Synthesis of $[\text{Hg}_4(\text{TePh})_7\text{IPy}]_n$ (**1**)

A mixture of $\text{Hg}(\text{TePh})_2$ (0.477 g, 0.78 mmol), $\text{CdI}_2(\text{PPh}_3)_2$ (0.222 g, 0.25 mmol) in 10 mL tetrahydrofuran (THF), under Ar atmosphere, was stirred for 1 h at 30 °C. The crude product was separated by filtration and dissolved in pyridine (15 mL) at 60 °C. After 4 days, stable orange crystals of **1** were formed. Yield: 0.429 g, 80%. Melting point: 135–138 °C. *Anal. Calc.* for $\text{C}_{47}\text{H}_{40}\text{Hg}_4\text{I}\text{NTe}_7$ (2441.26): C, 23.12; H, 1.65. Found: C, 23.15; H, 1.62%. Atomic ratios given by EDX analysis: $\text{Hg}_4\text{Te}_7\text{I}_1$.

3.2.2. Synthesis of $[\text{Hg}_8\text{Te}(\text{TePh})_{14}(\text{PPhMe}_2)_2] \cdot 0.5\text{DMF}$ (**2**)

PPhMe_2 (0.073 g, 0.4 mmol) was added to a solution of $\text{Hg}(\text{TePh})_2$ (0.152 g, 0.25 mmol) in 10 mL DMF and the mixture was placed into an ultrasonic bath at 35 kHz. The reaction was carried out under ultrasonication for 30 min at room temperature to give a deep-red solution. After 3 days stable red crystals of **2** were formed. Yield: 0.135 g, 83%. Melting point: 127 °C. *Anal. Calc.* for $\text{C}_{102}\text{H}_{99}\text{Hg}_8\text{NOP}_2\text{Te}_{15}$ (4947.49): C, 24.82; H, 1.95; N, 0.14. Found: C, 24.76; H, 1.98; N, 0.17%. Atomic ratios given by EDX analysis: $\text{Hg}_8\text{Te}_{15}\text{P}_2$.

3.2.3. Synthesis of $[\text{Hg}_{11}(\text{TePh})_{18}\text{Te}_2\text{Py}_3]_n$ (**3**)

PPh_3 (0.132 g, 0.50 mmol) was added to a suspension of $\text{Hg}(\text{TePh})_2$ (0.152 g, 0.25 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.066 g, 0.25 mmol) in 10 mL of pyridine. The mixture was stirred for 1 h at 65 °C under Ar atmosphere. The solid phase was removed by filtration, and after 3 weeks the filtrate afforded red prismatic crystals of **3**. Yield: 0.062 g, 40%. Melting point (dec.): 126–128 °C. *Anal. Calc.* for $\text{C}_{153}\text{H}_{135}\text{Hg}_{11}\text{N}_3\text{Te}_{20}$ (6858.19): C, 23.14; H, 1.66; N, 0.66. Found: C, 23.21; H, 1.69; N, 0.70%. Atomic ratios given by EDX analysis: $\text{Hg}_{11}\text{Te}_{20}$.

4. Conclusions

The reaction of $\text{Hg}(\text{TePh})_2$ with various ligands under different conditions can be used to manage the size of the clusters, and the results of the syntheses presented in this paper show that the yields are remarkably good for some clusters. Probably the nanocluster **3** was formed via spontaneous self-assembly of the building blocks **1** and **2**. It is reasonable to assume that for the successful achievement of self-assembly reactions, the entire assembly must be able to undergo self-correcting processes to access the thermodynamically stable species. Several critical conditions need to be considered for the synthesis of nanoclusters under thermodynamic control.

The use of $\text{Hg}(\text{TePh})_2$ as a precursor for the preparation of nanoclusters represents a noteworthy available method, as well as an efficient complementary methodology for silyl reagents. Because this approach should be extensible to the synthons of the general formula $\text{M}(\text{ER})_n$, for which the examples $\text{M} = \text{Mg}, \text{Bi}, \text{Ga}, \text{In}, \text{Sn}, \text{Sb}, \text{Zn}, \text{Cd}, \text{Hg}, \text{Au}, \text{Yb}, \text{Zr}, \text{Hf}$; $\text{E} = \text{S}, \text{Se}, \text{Te}$; $\text{R} = \text{aryl}, \text{alkyl}$, have been reported [48,49], we predict that a systematic methodology with basis on Hg-organyl telluroate/selenolate reagents for the synthesis of binary and ternary clusters should be possible.

Acknowledgements

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Appendix A. Supplementary material

CCDC 748057, 748 058 and 748 059 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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